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FEASIBILITY STUDY OF CLATHRATES FOR FOR CARBON DIOXIDE REMOVAL

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ABSTRACT

The research carried out under contract no. NAS 1-8292 with NASA, Langley, during the period 13 September, 1968 through 12 March, 1969 involved the feasibility study on the use of clathration phenomenan for the regenerative removal of carbon dioxide from space cabin environments. Selected clathrate-host compounds with and without the presence of "promoter" compounds were examined for reversible clathration of carbon dioxide. The feed gas consisted of CO_2-air mixtures having CO_2 partial pressures of 4 mm and 8 mm mercury (0.5 and 1.0%) at a total pressure of 1 atmosphere. The methods of gas-solid interactions and liquid-phase crystallizations were employed in the clathration studies.

Experiments were conducted to determine the dynamic adsorption and desorption (occlusion and exclusion) characteristics of selected clathrates. Thermal regeneration of the clathrate was investigated at 80°C (176°F) and 97°C (206.6°F).

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INTRODUCTION

The phenomenon of clathration involves the physical occlusion (or encapsulation) of a wide variety of chemical species within the hollow cavities or channels of crystalline compounds. The included component is called the "guest", and the "cage" or encapsulating component is the "host". A clathrate compound is formed when one or more molecules of a "guest" is locked into the cage-like or channel-like structures of the host molecules. There are no bonding forces of the classical type involved in their formation. The encaged guest molecule is held stably by the host structure by virtue of its exact fit within the cavities of the host. The release of the encapsulated guest and thus the regeneration of the host clathrate involves considerable low energy in-put. Clathrate compounds consist of three classes of inclusion compounds viz., cage structures, layer complexes and tunnel structures. A number of candidate compounds selected from among the above mentioned three classes have been examined in this investigation for their regenerable CO_2-occlusion characteristics. Clathration reactions by solid-gas interactions as well as by solution-phase crystallizations were experimented in this study.

The objectives in this research were to determine whether clathration phenomenon could be utilized to obtain improvements in certain respects over the current regenerative CO_2 sorbers. Following are some of the important improvements that were considered desirable: (1) larger percent sorption of CO_2, (2) lower energy requirements, (3) stability in cyclic operation, (4) increased selectivity and (5) ease of handling.

Although the preparation of a few CO_2-clathrates have been reported in the literature, no work appears to have been undertaken to maximize the encapsulation or optimize their preparation. In view of the potential of the clathration concept for regenerative containment of CO_2, exploratory research has been undertaken.

The investigations which were carried out during the reporting period, 13 September, 1968 through 12 March, 1969 may be broadly outlined as follows:

1. CO_2 clathration investigations
   a. Gas-solid interaction method
   b. Solution-phase crystallization method
2. Regenerative characteristics of selected CO_2 clathrates
3. Adsorption-desorption profiles of selected clathrates.

CO_2 CLATHRATE INVESTIGATIONS

The abilities of a number of selected clathrate-host compounds to "interact" with and encapsulate carbon dioxide were investigated in a number of exploratory experiments. The solid-gas reaction method was first employed to study the clathrate formation reaction. In the beginning, very few experiments were carried out by following an equilibration procedure. Subsequently, the gas-flow method was adopted and, therefore, most of the experiments reported here were carried out by this latter technique.

Candidate Clathrate-Hosts. A number of clathrate-host compounds were selected from among the three classes of clathrates. The criteria for their selection were (i) their reported (literature) tendency to form CO2-clathrates, (ii) possibility of achieving high weight-percentages of CO_2 occlusion based on considerations of the molecular weights of guest and host components and their "molar combining ratios", (iii) possibilities of incorporating "promotor" compounds and (iv) the ease of their availability and handling. Table 1 lists the selected compounds and their classifications.

Table 1

Clathrate-Hosts for CO_2-Encapsulation Studies

Compounds	Classification
Urea	Channel Structure
Thiourea	Channel Structure
Urea-hexamethylene-diamine	Channel Structure
Urea-n-hexylamine	Channel Structure
Thiourea-cyclohexylamine	Channel Structure
Hydroquinone	Cage Structure
Hydroquinone-methanol	Cage Structure
Tetra (4-methylpyridino) Nickel (II) dithiocyanate	Coordination Compound
Hydrous oxides of Thorium, and Zirconium	Layer Structure

Feed Gas Composition. In order to simulate the conditions of space cabin environments, it was decided to use 0.5% and 1% CO_2 mixtures which correspond to CO_2 partial pressures of 4 mm and 8 mm of mercury respectively in all the clathration studies. A few experiments were carried out with 100% CO_2 gas. The total pressure was in all cases maintained at one atmosphere.

Temperature of Reaction. A number of the clathration experiments were carried out at three different temperatures, i.e., -6°C, 6°C and 25°C. After discussing with Mr. Rex Martin

of NASA, Langley, it was decided that all further experiments should be conducted at 25°C.

Experimental Methods

The initial experimental procedure for determining CO_2-sorption by Clathrate-hosts consisted of equilibrating 2.0-2.5 g of the (solid) clathrate-formers with the CO_2-containing feed (0.5%, 1.0%, or 100% CO_2-air mixtures) in a glass desiccator vessel for periods of 24 to 48 hours (batch equilibration). The desiccator was flushed several times and finally filled with CO_2-air mixture and the solid compounds allowed to equilibrate. The desiccator with the samples was maintained at the desired temperature during the period of equilibration. After equilibration, samples were withdrawn and analyzed for occluded CO_2. Most of the sorption experiments were done by using gas-flow method.

Figure 1 shows the schematic of a simple apparatus which was constructed for gas-flow method of CO_2-uptake by clathrate-hosts. It consisted of a number of glass spiral or U-tubes of 5 mm internal diameter, each of which was connected to the mainstream of the influent CO_2-air mixture through appropriate ball and socket joint connectors. The gas-flow velocity was measured at the end of each spiral tube with a detachable flow meter. The entire gas-flow adsorption unit consisting of four separate spiral tubes was then thermostated at the desired temperatures. Each of the spiral tubes was filled with the clathrate-host compound under consideration and the CO_2-air mixture passed at the desired velocity for the given duration of the experiment. It should be noted that this gas-flow unit is simple and easily adaptable to a number of experimental modifications such as temperature variations and continuous monitoring of the effluent gases from the individual spiral tubes containing different clathrate systems.

Analytical Technique. Samples of the CO_2-clathrate compounds were withdrawn at the end of each solid-gas reaction experiment and were analyzed by means of gas chromatographic and gravimetric methods.

Initially, a Burrell chromatographic equipment with thermionic emission detector was employed for the analysis. A stainless steel column, 20 ft x 1/8 in., packed with silica gel was used for the separation. Helium was the carrier gas and was run at a flow rate of 15 ml/minute. At this flow rate and at a column temperature of 65°C, CO_2 showed a retention time of approximately 5 minutes. The instrument was calibrated for carbon dioxide by using 0.02 ml sample volume and measuring the integrated area under the peak. The amount of carbon dioxide in the calibration sample was calculated by using the relationship,

$$m = \frac{(MW)\ (P)\ (V)}{(R)\ (T)}$$

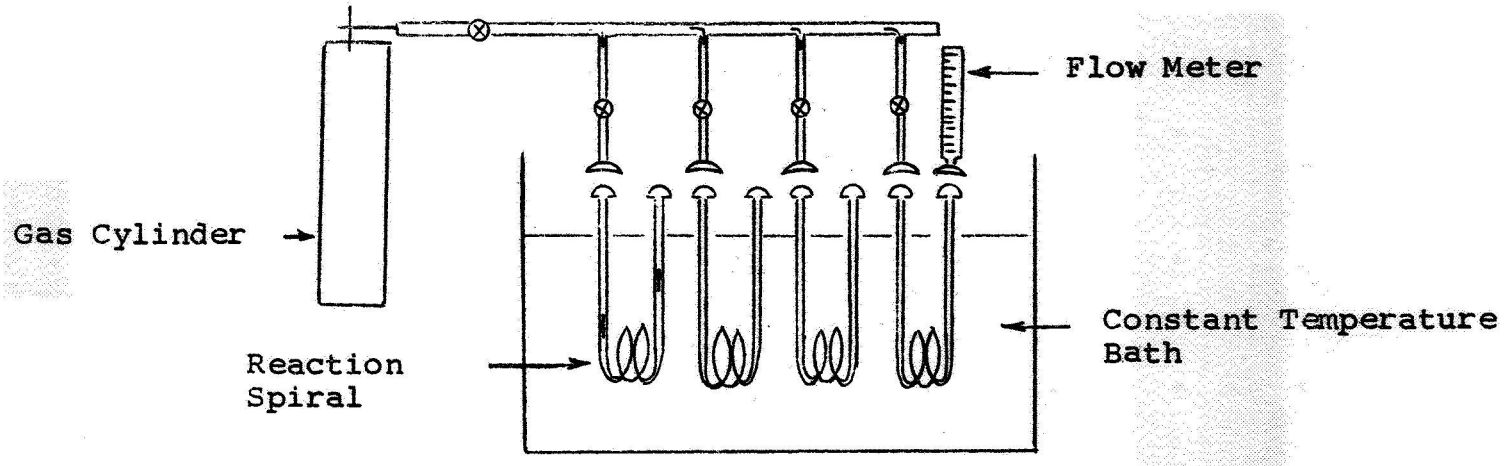

Figure 1

EXPERIMENTAL SET UP FOR CO_2 ADSORPTION BY FLOW METHOD

where

MW = molecular weight of CO_2
m = weight in grams of CO_2
P = pressure
V = volume
R = gas constant
T = absolute temperature

The sensitivity of the detector was calculated by using the equation

$$S = \frac{m}{\text{area under the peak for the standard sample}}$$

the solid CO_2 clathrate samples were inserted into a sample with a by-pass which allowed the carrier gas to go through the bypass loop, or through sample loop. Samples of 3 to 5 mg of CO_2-clathrates were weighed out on a small piece of aluminum foil, wrapped up tightly and then forced into the sample loop. The sample loop was then sealed, flushed with carrier gas and then heated to 150-160°C to release the occluded CO_2 from the clathrate crystals. The carbon dioxide peak was recorded. The area under this peak was compared with the calibration chart in order to estimate the amount occluded by the clathrate. During the latter portion of this research contract a Varian Aerograph (1800 series) instrument with thermal conductivity detector was used. CO_2 clathrate samples were pyrolyzed in order to desorb the occluded CO_2 for gas chromatographic analysis. Some of the details of the gas chromatographic operations are given below:

Column: Porapak Q; 6' x 1/4"
Column temperature: 65°C
Injector temperature: 165°C
Detector temperature: 170°C
Inductor temperature: 150°C and 80°C
Carrier gas: Helium
Flow of carrier gas: 60 ml/min

In the CO_2-sorption-desorption profile studies, effluent gas samples were withdrawn at regular intervals and were analyzed for their CO_2 content by the Varian Aerograph instrument.

A gravimetric method for the determination of CO_2-sorption in the sample clathrate was also utilized. This method depends upon the loss of weight due to the exclusion of CO_2 from the solid clathrates when treated with a known weight of acid. The procedure is recommended for the delinmination of CO_2 in solid compounds. In "Standard Methods of Chemical Analysis" by N.H. Furman (Sixth Edition, Vol. 1, p. 301). The apparatus used for this method was the Schroetter Alkalimeter. This method was found to be rapid and reproducible.

Clathration of CO_2 by Batchwise Equilibration

A few experiments were carried out in which the possible occlusions of CO_2 in clathrate-host structures were explored by employing batch equilibration technique described earlier in this report. Analysis of the resulting compounds after 24-48 hours of equilibration indicated very poor clathration characteristics. It should be noted that by employing the solid-gas equilibration procedure, pure hydroquinone, urea and thiourea hosts do not show any occlusion of CO_2 at all at the three temperatures of reaction, viz., 25°, 6°, -6°C. Urea-n-hexylamine and thiourea-cyclohexylamine clathrates show detectable adsorption of CO_2 at -6°C. In this preliminary series of experiments, the observed value of 2.6% (by weight) adsorption of CO_2 by urea-hexamethylenediamine (HMDA) falls far below the expected hypothetical values which are calculated on the basis of an assumed ratio of 1:3 for CO_2 host molecules. It should be pointed out that the equilibration procedure adopted in the current series is by no means the most effective one for CO_2-sorption. An alternative method of passing the gas through glass spiral or U-tube packed with the clathrate host (Figure 1) was adopted for the rest of the occlusion studies. More intimate and effective contact is made between the reactants, in this technique. The results observed in the equilibration method could at best be taken as a strong qualitative tendency exhibited by the clathrate host for the uptake of CO_2. Table 2 illustrates the results of gas-solid interaction experiments of clathrate hosts with pure carbon dioxide at 25°C and 6°C. The urea-hexamethylene-diamine clathrate shows significant uptake of CO_2 relative to the other host compounds.

Clathration of CO_2 by Gas-Flow Method

By using 1% and 0.5% CO_2-air mixtures as the influent feed gases, the CO_2 occlusion characteristics of the clathrate host compounds were investigated in separate series of experiments. In both these series of experiments, the influent gas was passed through $CaCl_2$-tube prior to reaction with the clathrate-formers. In the case of 1% CO_2 feed, experiments were carried out at -6, 6 and 25°C and in the case of 0.5% the uptake experiments were done at 6 and 25°C. In each case the reaction consisted in passing the influent gas through each clathrate-host (about 6 g) packed in the individual spiral tube at a flow rate of 10 cc per minute for 6 hours. At the end of the reaction, the substrate clathrate compounds were removed from the spiral tubes and analyzed for their CO_2 contents by means of gravimetric method. Values of weight percentages of CO_2-occluded on the basis of the total weights of the clathrates were computed. Results obtained from 1% CO_2 feed experiments are presented in Table 3 and those obtained from the 0.5% CO_2 feed experiments are given in Table 4.

Consideration of the results of the 1% CO_2 influent experiments indicates that urea and urea-n-hexylamine systems gave the largest CO_2-uptake values (viz., 7.6 and 9.6% respectively) among

Table 2

Clathration of Carbon Dioxide by Solid-Gas Reactions
Method: Batchwise Equilibration
Gas = Pure CO_2 (100%); Total pressure = 1 atm.

Compounds	Uptake of Carbon Dioxide Percent (wt) 25°C	6°C
Hydroquinone	CO_2 not detected	1.8
Urea	CO_2 not detected	1.4
Thiourea	CO_2 not detected	1.2
Hydroquinone-methanol	CO_2 not detected	0.5
Urea-hexamethylenediamine	3.2	13.9
Thiourea cyclohexylamine	0.1	5.3
Tetra(4-methyl-pyridino)Ni(II)-dithiocyanate	---	2.5

Table 3

Adsorption of Carbon Dioxide
by Clathrate-Forming Compounds

Influent gas = 1% CO_2; rest = air;
reaction time = 6 hrs; flow = 10 cc/min.

Clathrate Hosts	Percent Adsorption of CO_2 (by weight)		
	-6°C	+6°C	25°C
Hydroquinone	3.1	1.4*	1.3
Urea	3.3	5.5, 6.4*	7.4
Thiourea	4.7	2.7*	3.0
Tetra(4-methyl-pyridino) Ni(II)-dithiocyanate	3.8	2.8, 6.6*	1.7
Urea-hexamethylenediamine	6.0	2.6, 2.9	2.8
Urea-n-hexylamine	5.8	2.6, 2.9	9.6
Thiourea-cyclohexylamine	3.4	2.7, 3.0	6.9

*Reaction time = 24 hrs Flow rate = 80 cc/min.

Table 4

Adsorption of Carbon Dioxide by Clathration

Influent gas = 0.5% CO_2; rest = air;
reaction time = 6 hrs; flow = 10 ml/min.

Clathrate Hosts	Percent Adsorption of CO_2 (by weight)	
	+6°C	25°C
Urea	7.2	2.9
Thiourea	3.5	1.7
Hydroquinone	3.9	3.2
Tetra(4-methylpyridino) Ni(II)-dithiocyanate	1.9	2.9
Urea-hexamethylenediamine	6.5	4.1
Urea-n-hexylamine	7.1	5.3
Thiourea cyclohexylamine	11.9	2.2
Hydroquinone-methanol	2.9	3.5

the clathrates examined. Thiourea and thiourea-cyclohexylamine have shown 3.0 and 6.9% CO_2-uptake. The hydroquinone system is found to be relatively less satisfactory. It should be mentioned that the percent uptake values are by no means optimum and these are evaluated only to examine a number of systems rapidly on an exploratory basis. A number of appropriate parameters would have to be examined in order to determine the potential of any selected clathrate system. Results of adsorption studies from 0.5% CO_2 feed indicate that at 6°C thiourea-cyclohexylamine showed the largest value, 11.9%. Urea showed 7.2% uptake even in the absence of any "promotor" amine, whereas thiourea gave only 3.5% uptake in the absence of any amine. It should be noted that no attempt is made at present to rationalize any trends in the CO_2-uptake characteristics of the clathrates as a function of temperature, since the several important variables that affect the gas-solid reactions are not being examined in this study. However, the significant observation that emanates from the present feasibility study is that both urea and thiourea exhibit relatively satisfactory adsorption characteristics for CO_2 from 0.5 and 1.0% CO_2 feed gas.

Adsorption of CO_2 by Metal Hydrous Oxides

Since metal hydrous oxides can be considered as belonging to the class of inclusion compounds with layer structures, a few of these compounds were examined for their CO_2-uptake properties. Thorium, zirconium and lanthanum hydrous oxides were tested in this series by using 1% CO_2-air mixture as the feed. The metal hydrous oxides were precipitated by reacting the respective nitrates with ammonium hydroxide. The precipitates were then washed free of ammonia and dried at 90°C. The dried hydrous oxides were then activated by vacuum drying at 90-100°C. Samples of the hydrous oxides of thorium, thorium-calcium, lanthanum and zirconium-calcium thus prepared were then loaded into the reaction-spiral tubes. The influent gas containing 1% CO_2 was then passed through them at a flow rate of 10 ml/minute for 6 hours. Values of percent uptake of CO_2 were then determined gravimetrically and the results are presented in Table 5. Consideration of the data indicates that whereas thorium shows the largest percent adsorption at -6°C, the adsorption value obtained at room temperature was the largest for zirconium-calcium hydrous oxide. The data indicates that thorium, lanthanum and thorium-calcium hydrous oxides show a decreasing trend in their CO_2-adsorption with increasing temperature of reaction. Hydrous oxide of zirconium-calcium is seen to exhibit a nearly constant CO_2-adsorption at all three temperatures under consideration. A large number of experiments would have to be done involving several of the important parameters in order to be able to rationalize the trends. However, it should be stated that the preliminary data do indicate the promising nature of the metal hydrous oxides as potential candidates for reversible CO_2 removal.

Table 5

Adsorption of Carbon Dioxide by Metal Hydrous Oxides

Influent gas = 1% CO_2; rest = air;
reaction time = 6 hrs; flow = 10 ml/min.

Metal Hydrous Oxides	Percent Adsorption of CO_2 (by weight)		
	-6°C	+6°C	25°C
Thorium hydrous oxide	5.4	3.5	2.5
Thorium-calcium hydrous oxide	3.2	1.8	2.5
Lanthanum hydrous oxide	4.2	2.4	2.7
Zirconium-calcium hydrous oxide	3.6	3.7	3.8

Adsorption of CO_2 by Clathrate-Hosts in Presence of Moisture

Even in this type of preliminary feasibility study, it was considered necessary to evaluate the effect of the presence of moisture in the feed gas on the CO_2-occlusion characteristics of the selected clathrate hosts. Synthetic sodium alumino-zeolite which is one of the best among the previously reported CO_2-adsorbent is known to require a predrying step.

In this series of experiments, the effect of the presence of moisture on the CO_2-uptake characteristics of the clathrate host was investigated. The feed gas consisted of 0.5% and 1% CO_2-air mixtures. In each case the feed gas was premoisturized by bubbling through water at the desired temperature. The gas flow was maintained at 10 ml/minute for six hours. The percentages of CO_2-uptake was determined by gravimetric method described earlier. Results of the experiments thus carried out are presented in Table 6. Data on the CO_2-uptake by the clathrates in the absence of moisture are also included in Table 6 to provide comparison. In the case of 0.5% CO_2 feed, the presence of moisture has in general resulted in slightly increased CO_2-uptake percentages. The hydroquinone and thiourea-amine clathrates showed decreased values of CO_2-uptake in the presence of moisture. In the case of 1.0% CO_2

Table 6

Adsorption of CO_2 by Clathrate in Presence of Moisture

Reaction time = 6 hrs; gas flow = 10 ml/min; temperature = 25°C.

Clathrate Hosts	Percent Adsorption of CO_2 (by weight)			
	0.5% CO_2 with Moisture	0.5% CO_2 without Moisture	1% CO_2 with Moisture	1% CO_2 without Moisture
Urea	2.5	2.9	3.8	7.6
Thiourea	3.0	1.7	1.0, 2.4	3.0
Hydroquinone	0.9	3.2	0.5, 1.7	1.3
Tetra(4-methyl-pyridino)-Ni(II)-dithiocyanate	6.5	2.9, 4.9	0.8	1.7
Urea-hexamethylenediamine	5.4, 12.4	4.2, 4.0	4.8	2.8
Urea-n-hexylamine	5.3, 5.9	4.9, 5.6	5.3	9.6
Thiourea cyclohexylamine	1.8, 4.7	2.6, 1.9	1.9	6.9
Hydroquinone-methanol	0.5, 1.0	2.6, 3.5	4.3	3.7

feed, however, the values of CO_2-adsorption in the presence of moisture are somewhat smaller than in the absence of mois Urea and urea-amine clathrates have shown CO_2-uptake values 3.8 to 5.3%. In consideration of the results of the two ser of experiments, it may be stated that in spite of the preser of moisture in the influent feed, the clathrate compounds examined in this study do exhibit satisfactory CO_2-adsorptic characteristics. Investigation on the adsorption of CO_2 by the metal hydrous oxides were extended to include the examir tion of the effect of moisture content of feed gases. Resul obtained from these studies are presented in Table 7. Consi eration of the data in Table 7 indicates that although thor: hydrous oxide showed the highest percent of CO_2-adsorption : the absence of moisture among the hydrous oxides examined, : showed less than 1% adsorption in the presence of moisture. Zirconium and zirconium-calcium hydrous oxides showed satis: tory CO_2-adsorption characteristics (2.8 to 4.4%) in the pr sence of moisture. Further detailed and systematic studies are necessary before any conclusions regarding the CO_2-adso: tion characteristics of the different hydrous oxides can be arrived at.

Solution-Phase Crystallization Method

This method, in general, consists in interacting the guest component with a solution of the host in appropriate solvent and allowing the solid clathrate compounds to separ out. In the present studies, gaseous CO_2 (0.5% and 1% mixt was bubbled through a saturated solution (at room temperatu of the hosts viz., hydroquinone, urea, thiourea, metal chel and the promotor containing clathrate hosts in methanol. T reaction was allowed to take place at atmospheric pressure for 30-minute periods. At this time clathrate crystals sta appearing. They were then filtered and dried under mild su The CO_2-clathrates thus obtained were analyzed by the gravi method. Data obtained from these studies are presented in Table 8. In general, the data do not indicate any significa increases in the adsorption of CO_2 by the clathrate hosts i going from a 0.5% to 1.0% CO_2 mixture. In the cases of hyd quinone, urea and thiourea, a smaller CO_2-uptake was observ with 1% CO_2 mixture than with 0.5% CO_2. No conclusions car justifiably be drawn from these preliminary data regarding effect of varying the CO_2-air mixture on the percent uptake of CO_2 by the clathrate hosts. Urea shows 1.9 to 3.0% adsor of CO_2 even in the absence of any promotor amine. The addi of the promotor amine does not appear to bring about increa adsorption characteristics.

Table 7

Adsorption of CO_2 by Metal Hydrous Oxides

Reaction time = 6 hrs; flow = 10 ml/min.

Metal Hydrous Oxides	Percent Adsorption of CO_2 (by weight)			
	0.5% CO_2 6°C	0.5% CO_2 25°C	0.5% CO_2 with Moisture, 25°C	1.0% CO_2 with Moisture, 25°C
Thorium hydrous oxide	2.4	5.9	0.9	0.9
Thorium-calcium hydrous oxide	---	2.2	---	---
Lanthanum hydrous oxide	4.3	2.0	1.1	1.2
Zirconium-calcium hydrous oxide	2.0	4.3	4.4	2.0
Zirconium hydrous oxide	---	---	0.8	2.8

Table 8

Adsorption of CO_2 by Clathration by Solution-Phase Method

Clathrate Hosts	Percent Adsorption of CO_2 (by weight)	
	0.5% CO_2 Air Mixture	1.0% CO_2 Air Mixture
Urea	3.0	1.9
Thiourea	2.1	1.5
Hydroquinone	1.0	0.4
Tetra(4-methylpyridino)-Ni(II)-dithiocyanate	0.4	0.9
Urea-hexamethylenediamine	1.4	3.4
Urea-n-hexylamine	2.7	1.9
Thiourea-cyclohexylamine	0.9	1.7
Hydroquinone-methanol	0.9	---

Apart from the fact that comparatively smaller values are obtained in the liquid-phase method for CO_2-uptake, it is felt that this method may not lend itself to a convenient and efficient adaptation in the space cabin environments.

REGENERATION CHARACTERISTICS OF SELECTED CO_2 CLATHRATES

In a number of preliminary experiments, the release of the occluded CO_2 by means of thermal decomposition was examined. The clathrate compound was taken in a U-tube and heated at the desired temperature by keeping the U-tube in an appropriately thermostated bath. Nitrogen gas was allowed to flow through the U-tube during the heating so that the released CO_2 may be carried away from the system effectively. Heating was carried out for different periods and samples of the "decomposed" clathrates drawn for analysis. The samples were analyzed by gas chromatographic methods using thermal conductivity detector. Data obtained from thermal decomposition experiments of urea-hexamethylenediamine clathrate at two different temperatures are shown in Table 9. The CO_2 content of clathrate at the end of 2-hour, 5-hour and 6-hour periods were then determined (Table 9). These preliminary data indicate that 2-hour heating at 97°C results in the expulsion of more than 50% of the occluded CO_2 and at the end of 5 hours, the exclusion of CO_2 is nearly complete. The release of CO_2 has thus taken place without the melting of the clathrate. It should be pointed out that the optimization of the experimental conditions for the CO_2 release has not been attempted. The present preliminary study has only indicated that it is possible to release the occluded CO_2 much below the melting point of the clathrate. Results of thermal decomposition experiments at 80°C have indicated that after 6 hours the CO_2 contents of the clathrates have been brought down to 0.7 to 1.9%. However, the increased CO_2 content of the clathrate after a 2-hour heating over their initial CO_2 content is anamolous. The reasons for such anamolous behavior and the mechanism of the thermal decomposition can be ascertained only by detailed and systematic studies in a future program of research.

ADSORPTION-DESORPTION PROFILES OF SELECTED CLATHRATES

The exploratory studies discussed thus far in the report related to the CO_2-occlusion characteristics of a number of clathrate formers. These studies indicated the weight percentages of CO_2-adsorption by the candidate clathrates. However, in order to evaluate in a preliminary manner the possible application of the clathrate systems for the regenerative removal of CO_2 from space cabin environments, it was

Table 9

Removal of Adsorbed CO_2 by Thermal Methods

Clathrate compound = Urea-HMDA

Starting Material CO_2 Content %	CO_2 Content of the Clathrate after Heating at 80°C		CO_2 Content of the Clathrate after Heating at 97°C	
	2 hrs	6 hrs	2 hrs	5 hrs
7.8	8.2	0.6	3.3	0
6.0	9.1(?)	2.0	2.9	0
7.6	9.6(?)	0.9	-	-

considered desirable to carry out some profile studies on the adsorption and release of CO_2 by any selected clathrate hosts. The experimental technique for the study of the uptake profile consisted of passing the pre-moisturized CO_2-mixture (0.5% CO_2) through the clathrate host (urea-hexamethylenediamine) contained in a glass U-tube (Figure 1) at 50 ml and 100 ml/minute flow rates and at 25°C. The effluent gas emanating from the clathrate-containing tube was then sampled at periodic intervals of 15 minutes or less and analyzed by means of gas chromatographic technique using Varian Aerograph (1800 series) instrument with thermal condutivity detector. Figure 2 represents a typical gas chromatographic plot of CO_2 of effluent samples from adsorption profile study. CO_2-contents of the effluent gas samples were then computed. The CO_2-adsorption profile was traced by plotting the CO_2 contents of the effluent gases as a function of time. In order to investigate the CO_2-desorption profile the CO_2-containing clathrate from the adsorption-profile experiment was heated in a thermostated bath. Nitrogen was passed through the clathrate in order to flush the excluded CO_2. The effluent gas from the clathrate was then sampled periodically and analyzed gas chromatographically.

Figure 3 represents the results of a CO_2-adsorption profile study. The influent feed gas, which was 0.5% CO_2, was passed through an 8 g sample of urea-hexamethylenediamine at a flow

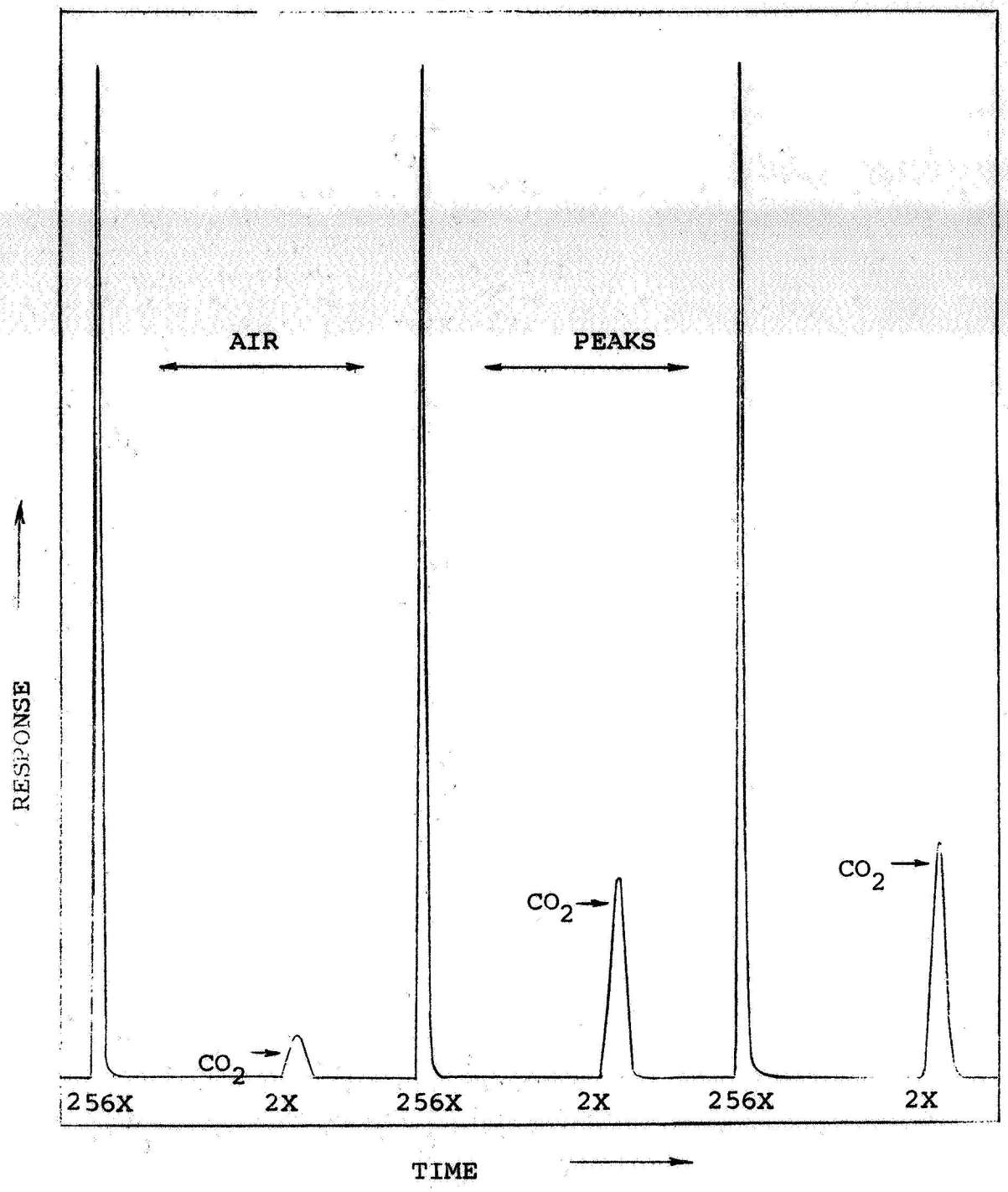

FIGURE 2

Typical gas chromatographic peaks at different times during CO_2-occlusion profile study, (Varian Aerograph, with T.C. detector).

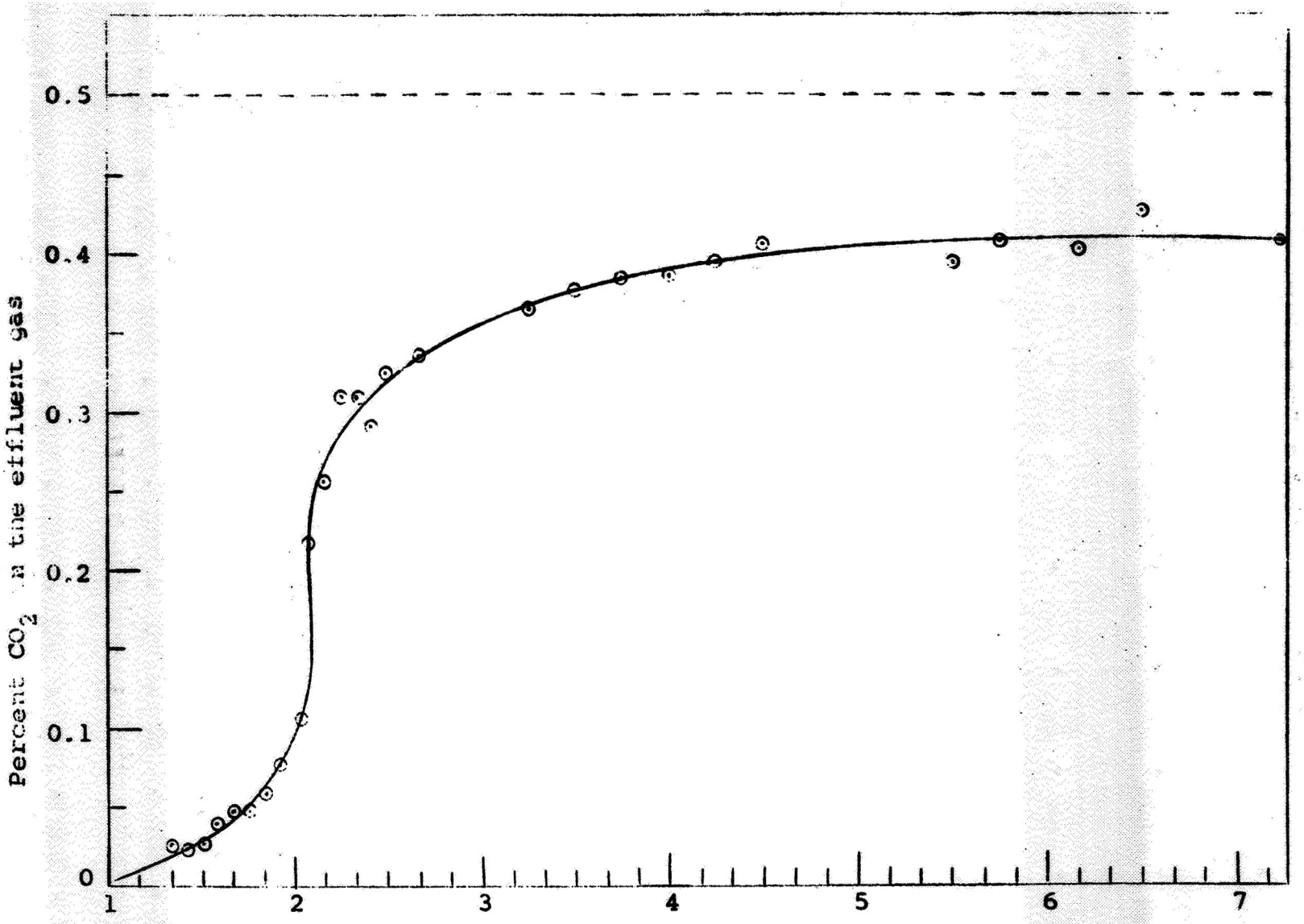

FIGURE 3

CO_2—occlusion profile of urea - HMDA clathrate: weight of clathrate = 5g; Feed gas = 0.5% CO_2; premoisterized flow rate = 100 ml/min.

rate of 100 ml/minute. During the first hour, the effluent gas did not show any appreciable CO_2. The effluent gas exhibited a CO_2 content of 0.1% only after 2 hours of passing through the clathrate. A sharp increase in the CO_2 content (0.25 to 0.3%) of the effluent was noticed after about 2 hours and 15 minutes. A steady state value of 0.39 to 0.4% CO_2 in the effluent gas was reached in approximately 4 hours. This value remained constant at that level throughout the remainder of the adsorption run (3-1/2 hours).

In the second experiment the CO_2 adsorption profile of the urea-hexamethylenediamine clathrate was investigated at a flow rate of 50 ml/minute using 0.5% CO_2 gas as the influent feed. Figure 4 illustrates the data obtained from this experiment. No CO_2 was detected during the first 6-hour period. The appearance of CO_2 in the effluent showed a gradual increase and it reached a sloping steady-state region between eight and nine hours of sorption run. The CO_2 content of the effluent at this steady-state region was 0.2 to 0.25%. A constant value of 0.35% CO_2 was attained after about 10 hours of passing.

An alternate adsorption profile experiment was carried out in order to check the reproducibility and also to follow it up with a CO_2-exclusion profile study. This experiment was run for nearly 4-1/2 hours (See Figure 5). Measureable CO_2 started appearing only at the end of about 2 hours. After about 3 hours 15 minutes, a sharp increase in the effluent CO_2 content (0.33% CO_2) was observed. A steady-state value of 0.38% CO_2 was reached at about 4 hours. The CO_2-sorbed clathrate was subsequently heated at 80° to release the CO_2. Nitrogen was passed at 8 ml/minute. A typical gas chromatographic plot of the effluents from CO_2-exclusion profile experiment is illustrated in Figure 6. The effluent profile (see Figure 7) shows that a value of 0.86-0.87% CO_2 in the effluent stream was attained after about 7 minutes of heating. The CO_2-content of the effluent tapered off to a value of 0.03% in less than 1 hour. The attainment of CO_2 contents such as 0.86-0.87% in the effluents relative to the 0.5 CO_2 content of the influent gas is indicative of the occurrence of a chromatographic banding effect on the columns. Carrier gas flow rates of 10 ml/minute and above resulted in more rapid and perhaps less complete exclusion of CO_2 from the clathrate. Some preliminary calculations were made on the "Half-life" efficiency (or breakthrough) of the urea-HMDA clathrate for CO_2-adsorption from 0.5% CO_2 feed gas. These data are presented in Table 10 along with those of another typical CO_2 sorber, the anion exchanger, IR 45. Although the results are not strictly comparable, they indicate that the urea-HMDA clathrate system does appear promising and warrants further detailed investigations.

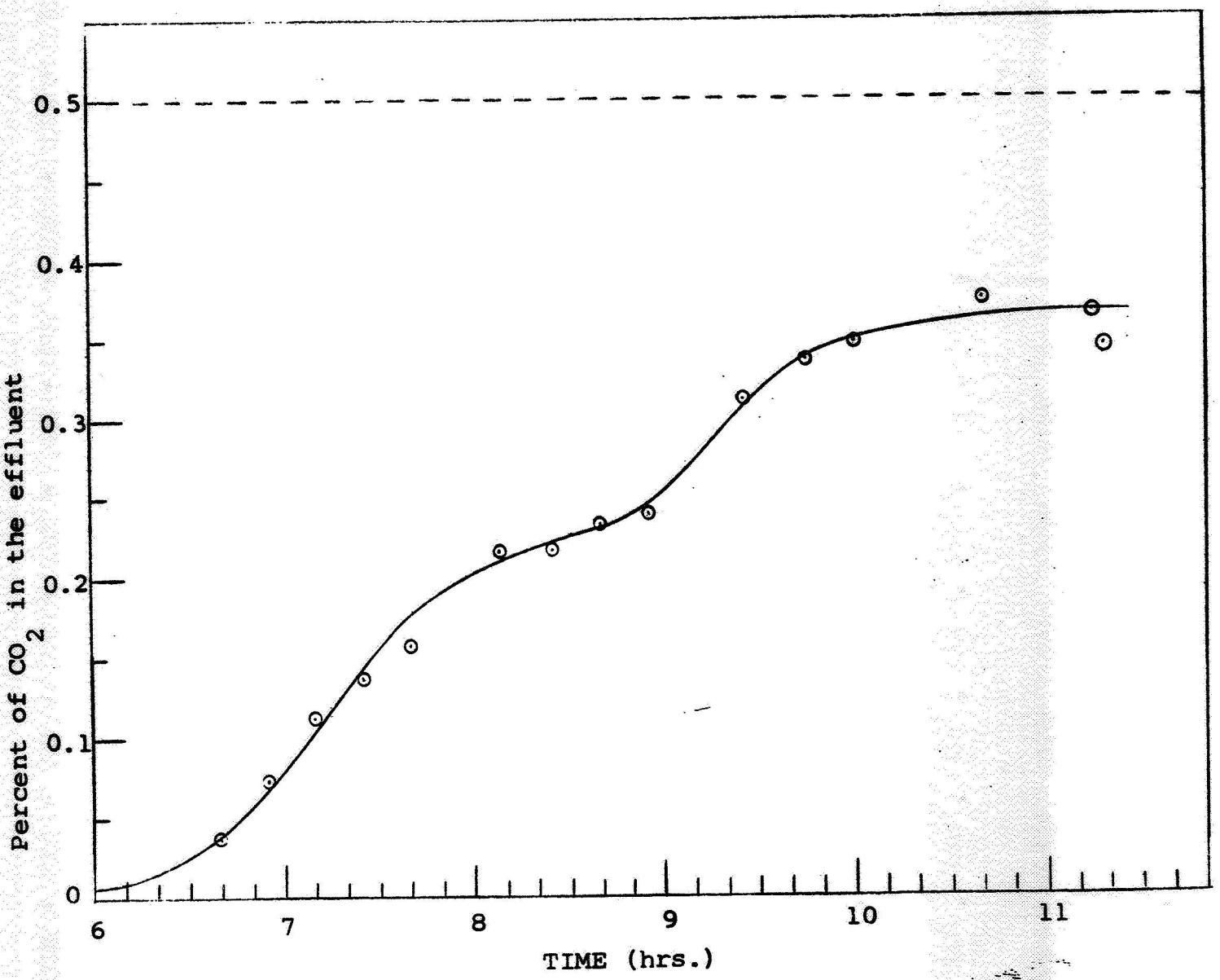

FIGURE 4

CO_2 - occlusion profile of urea - HMDA clathrate: Weight of clathrate= 5g; Feed gas= 0.5% CO_2, premoisterized; flow rate = 50 ml/min.

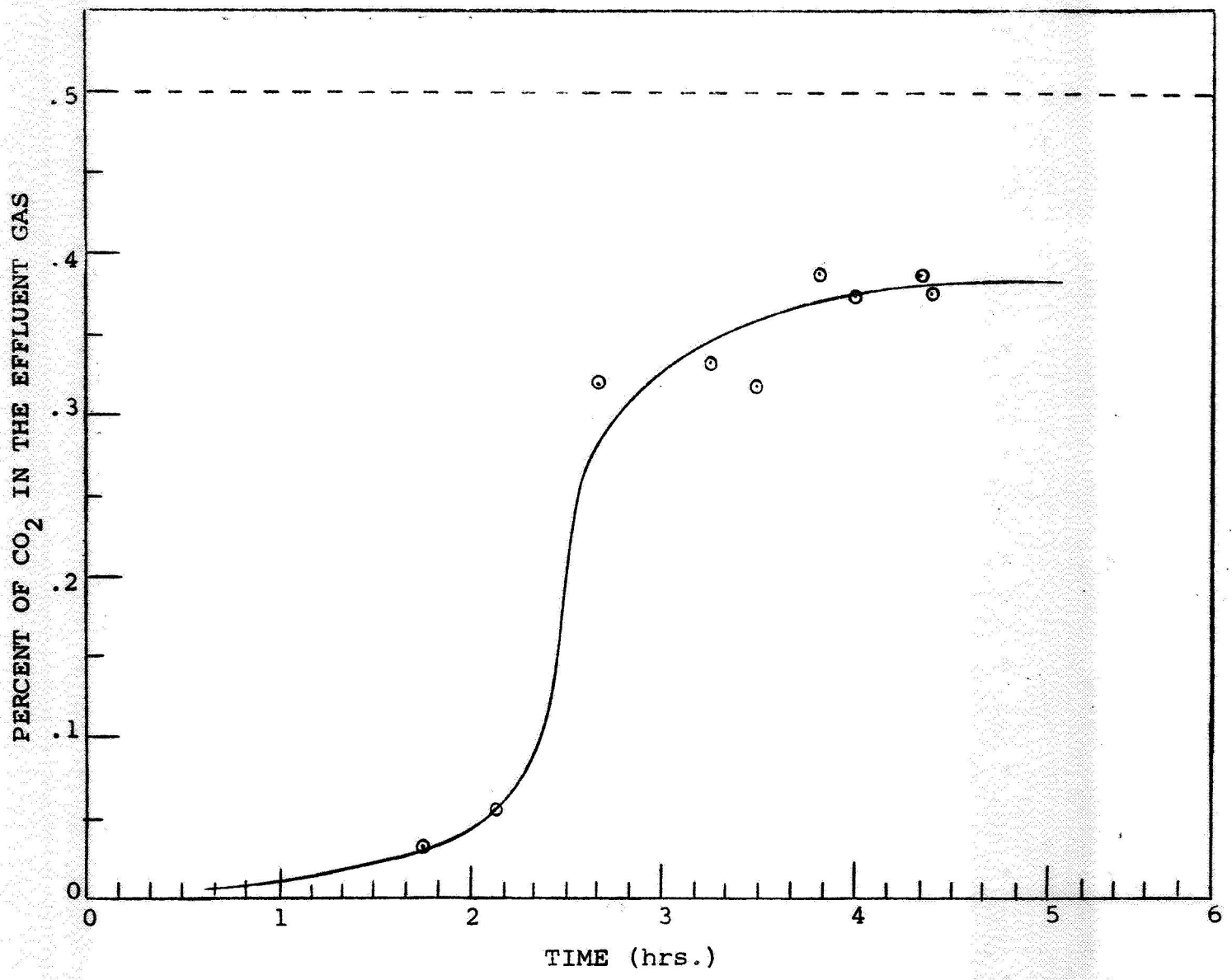

FIGURE 5

CO_2 - occlusion profile of urea - HMDA clathrate: conditions same as in Figure 1; testing reproducibility.

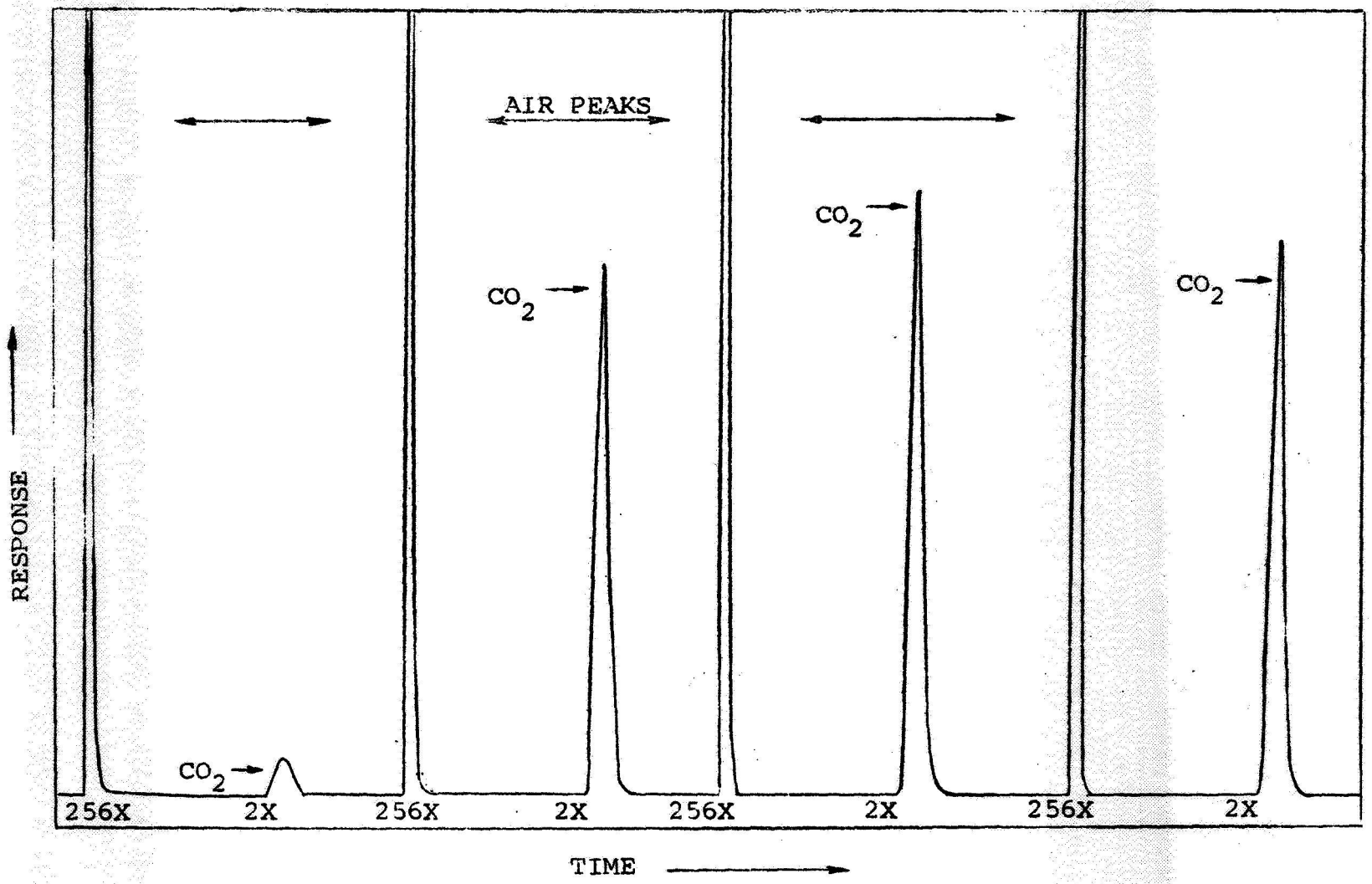

FIGURE 6

Typical gas chromatographic peaks at different times during CO_2-desorption profile study; (Varian Aerograph with T.C. detector)

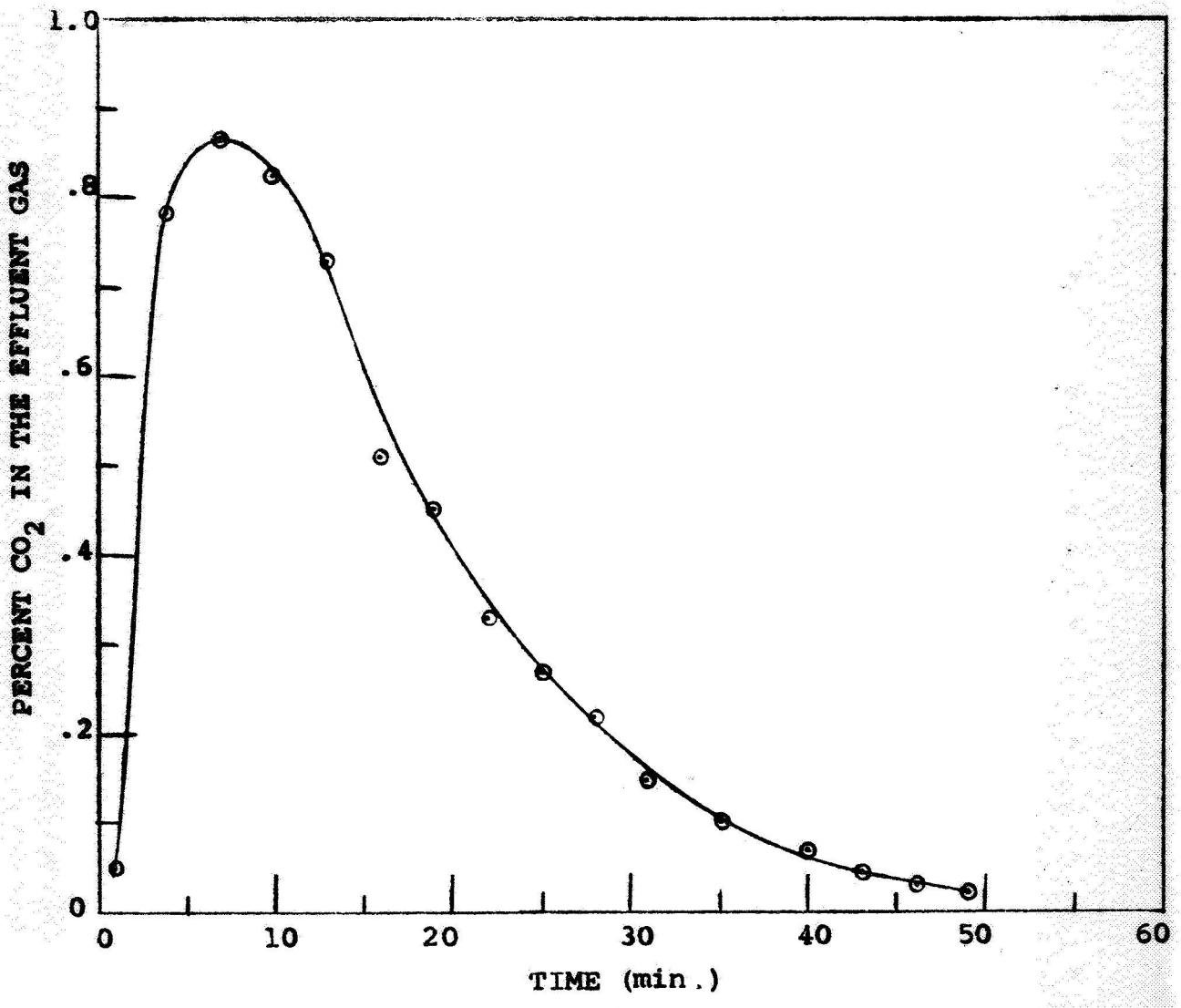

FIGURE 7

CO_2 desorption profile of urea - HMDA - CO_2 clathrate: weight of clathrate = 5 g; Temperature = 80°C; carrier gas = nitrogen; flow rate = 8 ml/minute.

Table 10

Carbon Dioxide Removal Characteristics on the Basis of Dynamic Studies

Adsorbent	Dry Weight of Adsorbent in the Experiment (g)	Water Content of the Adsorbent (%)	Wet Weight of the Adsorbent (g)	Flow Rate of Feed Gas ml/min	Half-Life (Time at Breakthrough)	Volume CO_2 Sorbed at Breakthrough* (liter/g)	Weight of CO_2 Sorbed at Breakthrough* (g/g)
Urea-HMDA	5	dry	5	50	9 hrs	0.0135	0.0265
Urea-HMDA	5	dry	5	100	130 min	0.0065	0.0128
IR 45‡	23.5	40	32.9	1000	112	0.0095	0.0187
IR 45	23.5	dry	23.5	1000	18	0.0015	0.0040

* The breakthrough point is the point at which the effluent gas shows 0.25% CO_2 content

‡ The data on IR 45 are computed from the Final Report of MSA Research Corporation for NASA (Contract No. NAS1-5277).

It should be mentioned that the conditions of the CO_2 adsorption and desorption profile studies reported here are by no means optimum. Several of the important parameters that affect such dynamic solid-gas reactions should be examined. Gas chromatographic analysis of the "regenerated" samples from the desorption profile experiment showed appreciable amounts of entrained CO_2 which thereby indicated the incompleteness of the CO_2-exclusion. Systematic studies on the regeneration of the CO_2 clathrates will have to be undertaken under different conditions of reduced pressure, temperature and gas flows.

The results of the CO_2-adsorption-desorption profile studies are of a preliminary nature and can only be taken to indicate qualitatively the potential application of the clathrate system for regenerative removal of carbon dioxide.

CONCLUSIONS

Results of the feasibility study have indicated that among the candidate clathrate-host compounds examined, urea, tiourea, urea-hexamethylenediamine, urea-n-hexylamine and thiourea-cyclohexylamine are satisfactory. They have shown CO_2 adsorption values of 7% to 10% (by weight) at 25°C from predried feed gases of 0.5% and 1% CO_2. In the presence of moisture the adsorption values are in the range of 4 to 6% (by weight). The CO_2-adsorption characteristics of the hydrous oxides of thorium, zirconium and lanthanum (layer-structured clathrates) have been examined. They have shown CO_2-adsorption of 4.5% to 6.0% (by weight). Experiments on the clathration of CO_2 by liquid-phase crystallization procedure gave relatively poor results viz., 2.0% to 3.0% by weight.

Regeneration of the CO_2 occluded urea-hexamethylenediamine clathrate has been attempted by the thermal decomposition method at 80-97°C and at atmospheric pressure. In this preliminary experiment, a nearly complete exclusion of CO_2 has been achieved in about 6 hours. It is felt that more detailed and systematic experiments are required in order to optimize CO_2-exclusion from the clathrates.

Preliminary experiments on the dynamic CO_2-adsorption desorption profiles of urea-hexamethylenediamine clathrate system have been carried out. At a 50 ml/minute flow rate of the influent gas (0.5% CO_2), no CO_2 is detected for the first 6 hours. A steady-state value of 0.2-0.25% CO_2-uptake is shown between 8 and 9 hours of passing of the feed gas. This corresponds to a CO_2-pick-up value of 0.0265 g CO_2 per gram of dry clathrate. At a 100 ml/minute flow rate, measurable CO_2 started appearing in the effluent only after 2 hours and a steady-state value of 0.38% in the effluent is found only after about 4 hours of passing. The CO_2-pick-up capacity at breakthrough in this case is 0.0128 g CO_2 per gram of dry clathrate.

Although the uptake profile data appear promising, considerable amount of systematic work is needed to develop a reproducible system. The exclusion profile study has shown that a value of 0.86% to 0.87% CO_2 is detected in the effluent gas after less than 10 minutes of heating under atmospheric pressure. This CO_2-content of the effluent gas decreased to a value of 0.03% in less than 1 hour. Above all, the complete exclusion of CO_2 from the clathrate does not appear to have taken place.

SUMMARY

Studies were undertaken in order to explore the feasibility of using clathration phenomenan for the regenerative removal of carbon dioxide from space cabin environments. Preliminary clathration experiments were conducted with a number of selected clathrate-host compounds using 0.5% and 1% CO_2 as feed gases. Both gas-solid and solution-phase crystallization methods were employed in the preliminary clathration studies. Among the clathrate host compounds examined, urea, thiourea, urea-hexamethylenediamine, urea-n-hexylamine, thiourea-cyclohexglamine have been found to be satisfactory clathrate-formers with CO_2-occlusion values of 7% to 10% (by weight) at 25° from feed gases having 4 mm and 8 mm partial pressures of CO_2. In the presence of moisture, the clathrate-hosts showed 4-6% (by weight) of CO_2-adsorption. Hydrous oxides of thorium, zirconium and lanthanum were found to exhibit 4.5 to 6.0% (by weight) adsorption of CO_2 under the above conditions. Clathration experiments by the solution-phase crystallization method yielded relatively lower adsorption (2.0 to 3.0% by weight) of CO_2.

The dynamic adsorption-desorption characteristics of selected clathrates were investigated. At a 50 ml/minute flow rate of the influent gas (0.5% CO_2), urea-hexamethylene-diamine clathrate showed a CO_2 pick-up value of 0.0265 g CO_2 per gram of the compound at breakthrough point. When the flow rate was increased to 100 ml/min, a CO_2 pick-up value of 0.0128 g/g of the clathrate was obtained. Regeneration of the selected CO_2-clathrates was investigated at 80°C and 97°C.

RECOMMENDATIONS FOR FUTURE RESEARCH

On the basis of preliminary investigations concerning the possible applications of the clathration phenomenon for regenerative encapsulation and removal of CO_2 from space cabin environments, the following clathrate-host compounds appear promising: urea, thiourea, urea-hexamethylenediamine (HMDA), urea-n-hexylamine (HA), and thiourea-cyclohexylamine (CHA). Detailed and systematic studies of the clathration approach therefore are considered necessary and worthwhile. Preliminary results have indicated that the desorption of the encapsulated CO_2 from the urea-HMDA-CO_2 clathrate could be effected by thermal methods. The results of preliminary experiments on the dynamic CO_2-adsorption-desorption profiles of the urea-HMDA-CO_2 clathrate system appeared somewhat satisfactory. However, a considerable amount of systematic work is needed to develop a reproducible clathrate system.

In order to explore fully the potential of the clathration approach for the regenerative removal of CO_2, the following program of research is outlined:

1. Developmental research on the clathration of CO_2 by urea and related compounds.
2. Thermal decomposition characteristics of CO_2-clathrates.
3. CO_2-adsorption-desorption profiles of the clathrates.
4. Improvements in the application of synthetic zeolites and organic ion exchangers for reversible CO_2-adsorption.
5. Considerations of power requirements.

Details of the proposed research are delineated briefly below:

1. Clathration of CO_2

a. Urea and related compounds

Systematic studies will be undertaken for the reversible clathration of CO_2 by means of the host compounds which were found promising in our earlier feasibility study. Promoter compounds other than the amines considered in our earlier studies will be examined and thus some new clathrate-host compounds prepared and tested. Appropriate and important parameters that affect CO_2-clathration will be investigated. These variables include: (i) concentration and compositions of influent gas (ii) moisture content (iii) gas flow velocity (iv) particle size of the clathrate hosts (v) temperature of the clathration reactions and (vi) dimensions of the clathrate-host columns, i.e., ratio of diameter/length.

Clathration studies will also include physical-chemical examination of the resultant CO_2-clathrates for the nature of encapsulation. Infrared and x-ray methods will be used to obtain information regarding the nature of encapsulation. It is believed that these data could be useful in the solution of problem areas

and in bringing about efficient clathration reaction.

2. Thermal Decomposition of Clathrates

By means of thermogravimetric and differential thermal analysis methods it is proposed to examine the thermal decomposition patterns of the CO_2-clathrates. Results of these studies would provide experimental conditions for carrying out the decomposition of the clathrates under atmospheric and reduced pressure conditions. Besides, the stabilities of the clathrates under conditions of CO_2-desorption could be evaluated.

3. Dynamic CO_2-Adsorption-Desorption Profiles of Clathrates

On the basis of results obtained in 1 and 2 above, selection of clathrate host composition and useful range of experimental conditions will be made for the dynamic profile study. The adsorption-desorption profiles of the selected clathrate compounds will be investigated under conditions of (a) different CO_2-feed gas concentrations (b) gas flow velocities (c) moisture content of the feed gas (d) ratios of diameter to length of clathrate beds and (e) temperature.

In this phase, the regeneration and recycling characteristics of the selected clathrate systems will be investigated. These studies will provide important data that are useful for the evaluation of power requirements.

4. Developmental Work on Ion Exchangers and Molecular Sieves

In the course of my discussions with Mr. Rex Martin at NASA Langley on March 5, 1969, possible improvements in the existing CO_2-sorbers viz., molecular sieves and organic anion exchangers were considered. It was felt that investigations could be undertaken that would involve the preparation of appropriately doped molecular sieve material and studying its CO_2-adsorbing properties. Alternately, several methods of pretreatment of the molecular sieve should be investigated and then their CO_2-sorbing properties examined. The possibility of CO_2-adsorption by weakly basic anion exchangers should be explored in the absence of moisture. In addition to pretreatments, the possibility of restructuring of the polymeric base exchanger should be explored. This phase of the work will be planned in consultation with the sponsor.

5. Power Requirements

For any one or more of the finally-selected clathrate systems, it is proposed to make a preliminary evaluation of the power requirements.

Respectfully submitted,
IIT Research Institute

K.S. Rajan
Research Chemist

Approved by:

E.S. Freeman
Assistant Director,
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